

FORM PTO 1399  
(REV 5-99)

US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY DOCKET NUMBER  
2001\_0133ATRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. §371U.S. APPLICATION NO.  
(of PCT/JP99/04349)  
NEW 097762582International Application No.  
PCT/JP99/04349International Filing Date  
August 11, 1999Priority Date Claimed  
August 11, 1998

## Title of Invention

SUBSTRATE PLATING METHOD AND APPARATUS

## Applicant(s) For DO/EO/US

Akihisa HONGO, Naoki OGURE, Hiroaki INOUE, Satoshi SENDAI, Tetsuma Ikegami, Koji MISHIMA, Shuhei  
OKUYAMA, Mizuki NAGAI, Ryoichi KIMIZUKA and Megumi MARUYAMA

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:


1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. §371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. §371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. §371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau. - (Form PCT/IB/308) Attachment "A"
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. §371(c)(2)). - Attachment "B"
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c)(3)).
  - a. ☒ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19.
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. §371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. §371(c)(5)).

## Items 11. to 14. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98. - Attachment "C"
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment. - Attachment "D"
  - ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☒ Other items or information:

Unexecuted Declaration w/Cover Letter - Attachment "E"

Form PCT/IB/304 - Attachment "F"

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a. <input checked="" type="checkbox"/> A check in the amount of \$914.00 to cover the above fees is enclosed. A duplicate copy of this form is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. 23-0975 in the amount of \$_____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 23-0975.																				
<b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or          (b)) must be filed and granted to restore the application to pending status.</b>																				
19. CORRESPONDENCE ADDRESS  <div style="text-align: center;">   <b>000513</b>          PATENT TRADEMARK OFFICE       </div>			By: <i>Michael S. Huppert</i> Michael S. Huppert, Registration No. 40,268  WENDEROTH, LIND & PONACK, L.L.P. 2033 "K" Street, N.W., Suite 800 Washington, D.C. 20006 Phone: (202) 721-8200 Fax: (202) 721-8250  February 9, 2001																	

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JCO5 Rec'd PCT/PTO 0 9 FEB 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of :  
Akihisa HONGO et al. : Attn: BOX PCT  
Serial No. NEW : Docket No. 2001\_0133A  
Filed February 9, 2001 :

SUBSTRATE PLATING METHOD AND APPARATUS  
[Corresponding to PCT/JP99/04349  
Filed August 11, 1999]

THE COMMISSIONER IS AUTHORIZED  
TO CHARGE ANY DEFICIENCY IN THE  
FEE FOR THIS PAPER TO DEPOSIT  
ACCOUNT NO. 23-0975.

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, DC 20231

Sir:

Prior to initial examination of the above-identified  
application, kindly amend the application as follows:

**IN THE CLAIMS:**

Kindly amend claims 3, 5-6, 8 and 11 as follows:

3. (AMENDED) A method or apparatus for plating a substrate  
according to claim 1, comprising in said electroless plating  
process or said electroless plating bath:

means for disposing a substrate to be plated in such a  
state that a surface to be processed thereof faces upwardly, and  
forming a hermetically sealed space by said surface to be  
processed; and

plating liquid supply means for supplying an electroless plating liquid to said hermetically sealed space to perform an electroless plating process.

5.(AMENDED) A method or apparatus for plating a substrate according to claim 3, further comprising:

pressure pulsation means for generating a pressure in said hermetically sealed space that is higher than atmospheric pressure and for pulsating said pressure.

6.(AMENDED) A method or apparatus for plating a substrate according to claim 3, further comprising a preparation bath disposed in the vicinity of said hermetically sealed space or supplying said minimum amount of prepared electroless plating liquid to said hermetically sealed space just prior to the electroless plating process.

8.(AMENDED) A method or apparatus for plating a substrate according to claim 1, wherein said plating liquid used in said electroless plating process or said electroless plating bath comprises copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) having a concentration of 100 to 250 g/l, sulfuric acid ( $\text{H}_2\text{SO}_4$ ) having a concentration of 10 to 100 g/l, and chlorine ions having a concentration of 0 to 100 mg/l.

11.(AMENDED) A method for plating a substrate according to claim 1, wherein said plating liquid used in said method does not include an alkali metal as a pH regulator.

**Kindly add the following new claims:**

--12.(NEW) An apparatus for plating a substrate according to claim 2, comprising in said electroless plating process or said electroless plating bath:

means for disposing a substrate to be plated in such a state that a surface to be processed thereof faces upwardly, and forming a hermetically sealed space by said surface to be processed; and

plating liquid supply means for supplying an electroless plating liquid to said hermetically sealed space to perform an electroless plating process.

13. (NEW) An apparatus for plating a substrate according to claim 12, wherein the minimum amount of electroless plating liquid required for performing a predetermined plating on said substrate to be plated is supplied to said hermetically sealed space, and the electroless plating process is performed with said electroless plating liquid in a static state.

14.(NEW) An apparatus for plating a substrate according to claim 12, further comprising:

pressure pulsation means for generating a pressure in said hermetically sealed space that is higher than atmospheric pressure and for pulsating said pressure.

15.(NEW) An apparatus for plating a substrate according to claim 13, further comprising:

pressure pulsation means for generating a pressure in said hermetically sealed space that is higher than atmospheric pressure and for pulsating said pressure.

16.(NEW) An apparatus for plating a substrate according to claim 12, further comprising a preparation bath disposed in the vicinity of said hermetically sealed space for supplying said minimum amount of prepared electroless plating liquid to said hermetically sealed space just prior to the electroless plating process.

17.(NEW) An apparatus for plating a substrate according to claim 13, further comprising a preparation bath disposed in the vicinity of said hermetically sealed space for supplying said minimum amount of prepared electroless plating liquid to said

hermetically sealed space just prior to the electroless plating process.

18.(NEW) An apparatus for plating a substrate according to claim 14, further comprising a preparation bath disposed in the vicinity of said hermetically sealed space for supplying said minimum amount of prepared electroless plating liquid to said hermetically sealed space just prior to the electroless plating process.

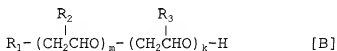
19.(NEW) An apparatus for plating a substrate according to claim 16, wherein said electroless plating liquid is processed as a waste liquid without circulating said electroless plating liquid after performing the electroless plating process with said minimum amount of electroless plating liquid.

20.(NEW) A method or apparatus for plating a substrate according to claim 2, wherein said plating liquid used in said electroless plating process or said electroless plating bath comprises copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) having a concentration of 100 to 250 g/l, sulfuric acid ( $\text{H}_2\text{SO}_4$ ) having a concentration of 10 to 100 g/l, and chlorine ions having a concentration of 0 to 100 mg/l.

21. (NEW) An method for plating a substrate according to claim 20, wherein said electrolytic plating liquid further comprises at least 0.14 to 70  $\mu\text{mol/l}$  of a sulfur compound expressed by a formula in [A] below, 10 to 5000 mg/l of a macromolecular compound expressed in a formula [B] below, and 0.01 and 100 mg/l of a nitrogen compound;

wherein L is an alkyl group having a carbon number of 1 to 6 which is substituted by a lower alkyl group, a lower alkoxy group, a hydroxyl group, or a halogen atom; and X is a hydrogen atom, a  $-\text{SO}_3\text{M}$  group, a or a  $-\text{PO}_3\text{M}$  group (M indicating a hydrogen atom, an alkali metal atom, or an amino group) in the formula [A]; and

R1 indicates a residue of a higher alcohol group having a carbon number of 8 to 25, a residue of an alkyl phenol with an alkyl group having a carbon number of 1 to 25, a residue of an alkyl naphthol with an alkyl group having a carbon number of 1 to 25, a residue of a fatty acid amide having a carbon number of 3 to 22, a residue of an alklamine having a carbon number of 2 to 4, or a hydroxyl group; R2 and R3 indicate a hydrogen atom or a methyl group; and m and k indicate an integer from 1 to 100 in the formula [B].







**REMARKS**

The present Preliminary Amendment is submitted to delete the multiple dependency of claims 3, 5-6, 8 and 11, thereby placing such claims in condition for examination and reducing the required PTO filing fee.

Copies of the amended portion of the claims with changes marked therein is attached and entitled "*Version with Markings to Show Changes Made.*"

Respectfully submitted,

Akihisa HONGO et al.

By



Michael S. Huppert  
Registration No. 40,268  
Attorney for Applicants

MSH/kjf  
Washington, D.C.  
Telephone (202) 721-8200  
Facsimile (202) 721-8250  
February 9, 2001

CLAIMS

09/762582

JC05 Rec'd PCT/PTO 09 FEB 2001

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1. A method of plating a substrate to fill a wiring recess formed in a semiconductor substrate with plating metal, said method comprising:

performing an electroless plating process of forming an initial layer on a substrate; and

performing an electrolytic plating process of filling said wiring recess with plating metal while said initial layer serves as a feeding layer.

2. An apparatus for plating a substrate to fill a wiring recess in a semiconductor substrate with plating metal, said apparatus comprising:

an electroless plating tank for forming an initial layer on a substrate by electroless plating;

an electrolytic plating tank for filling said wiring recess with plating metal while said initial layer serves as a feeding layer; and

transfer means for transferring a substrate between said tanks.

3. A method ~~[or apparatus]~~ for plating a substrate according to claim 1 ~~or 2~~, comprising in said electroless plating process or said electroless plating bath:

means for disposing a substrate to be plated in such a state that a surface to be processed thereof faces upwardly, and forming a hermetically sealed space by said

surface to be processed; and

plating liquid supply means for supplying an electroless plating liquid to said hermetically sealed space to perform an electroless plating process.

5

4. A method ~~[or apparatus]~~ for plating a substrate according to claim 3, wherein the minimum amount of electroless plating liquid required for performing a predetermined plating on said substrate to be plated is  
10 supplied to said hermetically sealed space, and the electroless plating process is performed with said electroless plating liquid in a static state.

5. A method ~~[or apparatus]~~ for plating a substrate  
15 according to claim 3 ~~or 4~~, further comprising:

pressure pulsation means for generating a pressure in said hermetically sealed space that is higher than atmospheric pressure and for pulsating said pressure.

20 6. A method or apparatus for plating a substrate according to ~~any one of claims~~ <sup>claim</sup> 3 ~~through 5~~, further comprising a preparation bath disposed in the vicinity of said hermetically sealed space for supplying said minimum amount of prepared electroless plating liquid to said  
25 hermetically sealed space just prior to the electroless plating process.

7. A method ~~[or apparatus]~~ for plating a substrate

according to claim 6, wherein said electroless plating liquid is processed as a waste liquid without circulating said electroless plating liquid after performing the electroless plating process with said minimum amount of  
5 electroless plating liquid.

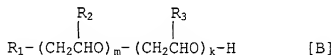
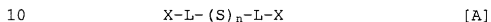
8. A method ~~[or apparatus]~~ for plating a substrate according to claim 1 ~~or 2~~, wherein said plating liquid used <sup>in</sup> said electroless plating process or said electroless plating  
10 bath comprises copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) having a concentration of 100 to 250 g/l, sulfuric acid ( $\text{H}_2\text{SO}_4$ ) having a concentration of 10 to 100 g/l, and chlorine ions having a concentration of 0 to 100 mg/l.

15 9. A method ~~[or apparatus]~~ for plating a substrate according to claim 8, wherein said electrolytic plating liquid further comprises at least 0.14 to 70  $\mu\text{mol/l}$  of a sulfur compound expressed by a formula in [A] below, 10 to 5000 mg/l of a macromolecular compound expressed in a  
20 formula [B] below, and 0.01 to 100 mg/l of a nitrogen compound;

wherein L is an alkyl group having a carbon number of 1 to 6 which is substituted by a lower alkyl group, a lower alkoxy group, a hydroxyl group, or a halogen  
25 atom; and X is a hydrogen atom, a  $-\text{SO}_3\text{M}$  group, or a  $-\text{PO}_3\text{M}$  group (M indicating a hydrogen atom, an alkali metal atom, or an amino group) in the formula [A]; and

R1 indicates a residue of a higher alcohol group

having a carbon number of 8 to 25, a residue of an alkyl phenol with an alkyl group having a carbon number of 1 to 25, a residue of an alkyl naphthol with an alkyl group having a carbon number of 1 to 25, a residue of a fatty acid amide having a carbon number of 3 to 22, a residue of an alkylamine having a carbon number of 2 to 4, or a hydroxyl group; R2 and R3 indicate a hydrogen atom or a methyl group; and m and k indicate an integer from 1 to 100 in the formula [B].



10. An apparatus for plating a substrate to fill a wiring recess formed in a semiconductor substrate with plating metal, said apparatus comprising:

one processing tank having an electroless plating liquid supply path for supplying an electroless plating liquid to form an initial layer on a substrate by electroless plating process, and an electrolytic plating liquid supply path for supplying an electrolytic plating liquid to fill said wiring recess by electrolytic plating while said initial layer serves as a feeding layer;

wherein the two paths are selectively switchable.

25

11. A method ~~for apparatus~~ <sup>claim</sup> for plating a substrate according to ~~any one of claims 1 through 10~~ <sup>1</sup>, wherein said plating liquid used in said method ~~for apparatus~~ does not

include an alkali metal as a pH regulator.

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**DESCRIPTION****SUBSTRATE PLATING METHOD AND APPARATUS****Technical Field**

5           The present invention relates to a method and apparatus for plating a substrate, and more particularly to a method and apparatus for plating a substrate to fill a wiring recess formed in a semiconductor substrate with wiring metal such as copper, copper alloy, or the like.

10

**Background Art**

Conventionally, in order to form a wiring circuit on a semiconductor substrate, a layer of Al or Al alloy is deposited on a surface of a substrate by a sputtering  
15 process or the like, and then unnecessary portions are removed from the layer by a chemical dry etching process using a photoresist or the like for a mask pattern. However, as the level of integration of circuits increases, the width of wiring becomes narrower to thus increase  
20 current density, resulting in generating thermal stress in the wiring and increasing temperature of the wiring. As a result, the layer of Al or Al alloy becomes thinner due to stress migration or electromigration, finally to cause a breaking of the wiring.

25           Hence, copper has been drawn much attention as a wiring material because of its lower resistance and higher reliability. However, it is difficult to form wiring by etching after a layer is deposited on a surface of a



substrate and then a patterning process is performed, differently from a conventional method using Al. Therefore, there has been attempted a damascene process in which a wiring groove is preformed in a substrate and filled with copper by chemical vapor deposition (CVD), sputtering, plating, or the like, and then unnecessary portions are removed from the surface of the substrate by chemical mechanical polishing (CMP), for thereby forming wiring in the groove.

Among these processes for filling a wiring groove with copper, the plating process has drawn much attention because of the following advantages. The processing cost is lower than that in other processes, and pure copper material can be obtained, and the process can be performed at such a low temperature that a substrate is not damaged. The plating process mainly comprises an electroless plating process, which is mainly performed by a chemical process, and electrolytic plating process, which is performed by an electrochemical process. The electrolytic plating process is generally more efficient than the electroless plating process.

Since copper is liable to be oxidized and corroded and diffused into  $\text{SiO}_2$ , wiring is generally formed after a wiring portion on a base material of the substrate is covered with a barrier layer of metal nitride such as  $\text{TiN}$ ,  $\text{TaN}$ , and  $\text{WN}$ . Since the sheet resistance of this barrier layer is prohibitively larger than the resistance of the plating liquid, it has been difficult to perform uniform

electrolytic plating on the barrier layer formed over the surface of the substrate.

Conventionally, a seed layer of copper is formed on the barrier layer by a sputtering process or a CVD process, and then plated with copper by an electrolytic  
5 plating process to fill fine recesses formed in the substrate with copper. However, it is difficult to uniformly deposit a layer on a wall of the fine recess by the sputtering process, and the CVD process introduces  
10 impurities into the deposited layer. Further, when the design rule is further decreased from about  $0.18\ \mu\text{m}$  to  $0.10\ \mu\text{m}$ , there is no dimensional margin to form a seed layer having a thickness of  $0.02$  to  $0.05\ \mu\text{m}$  within the recess.

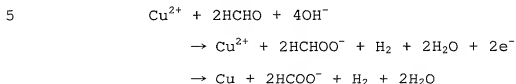
On the other hand, in the electroless plating  
15 process, since the plating layer is grown in isogonic directions from a side wall or a bottom surface of the fine recess, an inlet of the recess is covered with metal grown from the side wall and hence a void tends to be formed in the recess. In addition, since the plating rate of the  
20 electroless plating process is about one-tenth as slow as that of the electrolytic plating process, the electroplating process is inefficient.

#### **Disclosure of Invention**

25 It is therefore an object of the present invention to provide a method and apparatus for plating a substrate to form wiring by efficiently filling a fine recess formed in a semiconductor substrate with plating

metal without a void or contamination.

When formalin (HCHO) is used in the electroless plating process as a reducing agent, hydrogen gas (H<sub>2</sub>) is generated according to the following reaction.



When a plating surface of a substrate W faces downwardly or sideways, as shown in FIGS. 16A and 16B, bubbles 98 are generated by hydrogen gas (H<sub>2</sub>) in a plating liquid Q within recesses 42, such as fine grooves or the like, formed in the substrate, and these bubbles cause a plating defect 99. In order to prevent the generation of these plating defects 99, a pump or air is generally used to  
10            agitate the plating liquid in the conventional plating  
15            process. However, as shown in FIG. 16B, unevenly plated portions 100 are generated on a plating surface 97 of the substrate W in the direction that the hydrogen gas bubbles 98 move, indicated by the arrow A.

20            In order to remove the bubbles 98 from the plating surface 97, the conventional methods employ a jig to grip or suspend the plating substrate W, while a shock is applied externally to the jig to separate the bubbles from the plating surface 97. However, since there is risk that  
25            the shock will damage the jig or the plating substrate, this method is not desirable.

A conventional electroless plating apparatus comprises a plating processing tank and a plating liquid

circulating tank, and a plating liquid is circulated during the plating process. The plating liquid is prepared in a special preparation bath or in the circulating tank. Therefore, problematic reactions specific to the electroless copper plating, such as a Cannizzaro reaction or a disproportionation, occur in the electroless plating liquid immediately after preparation to cause deterioration of the plating liquid and changes in concentration of the plating liquid composition.

Accordingly, it is another object of the present invention to provide a method and apparatus for electroless plating which can minimize the amount of plating defects and unevenly plated portions and can prevent deterioration of a plating liquid and changes in concentration of the plating liquid composition to perform a plating process with a highly stable quality.

In the conventional electrolytic plating, in order to grow a uniform layer in through holes formed in a printed circuit board using copper plating, the concentration of copper in the plating liquid is lowered to improve the throwing power (in a high throwing power bath). This is because the overvoltage of a cathode is increased by increasing the polarization of the cathode to improve the throwing power. A degree of liquid flow through the holes can be expected when the dimensions of the holes in the printed circuit board are about 50 to 100  $\mu\text{m}$ .

The wiring grooves or holes formed in a surface of a semiconductor wafer have a width or diameter of 0.2  $\mu\text{m}$

or less and do not pass through the substrate. Hence, it is impossible to flow a liquid through such fine grooves or holes. Further, the electrophoresis speed generated by the electric field is numerically small, and hence the holes are filled with copper ions almost entirely by the diffusion of ion concentration. The amount of diffusion of copper ions in the holes decreases in proportion to the second power of the hole diameter (the area of the inlet of the hole) as the hole diameter decreases.

In contrast, the amount of deposition of copper ions in the hole grows smaller in proportion to the diameter of the hole. Accordingly, copper ions can be expected to be diffusion-controlled in grooves and holes, as semiconductor devices become more integrated and the width of grooves and diameters of holes become smaller in the future. When the hole diameters drop below  $0.15\ \mu\text{m}$ , in particular, copper ions tend to be diffusion-controlled depending on a methods of agitating plating liquid for a large aspect ratio.

Therefore, it is another object of the present invention to provide a method and apparatus of electrolytic plating capable of sufficiently filling a fine groove and a hole formed in a surface of a substrate using a copper plating without copper ions becoming diffusion-controlled in the groove and the hole, even when the width of the groove and the diameter of the hole become smaller and the integration in the semiconductor devices increases.

According to the present invention defined in claim 1, there is provided a method of plating a substrate

to fill a wiring recess formed in a semiconductor substrate with plating metal, the method comprising: performing an electroless plating process of forming an initial layer on a substrate; and performing an electrolytic plating process of  
5 filling the wiring recess with plating metal while the initial layer serves as a feeding layer.

With this method, an initial plating layer (seed layer) is formed with an electroless plating process, and then the recess in the substrate is filled with electrolytic  
10 plating metal while the initial layer serves as the feeding layer. Accordingly, an electroless plating process with high uniformity is combined with an electrolytic plating process having good qualities in leveling and high-speed filling. The recess having a barrier layer of a high  
15 electrical resistance can efficiently be filled with a void-free wiring metal, without the sputtering process or the CVD process in a series of plating processes. By filling the greatest portion of the recess formed on the feeding layer with the electrolytic plating, it is possible to maintain a  
20 high plating speed and increase throughput.

The electroless plating process and the electrolytic plating process may be performed in the same plating processing tank or in separate processing tanks. Further, the same plating liquid may be used in the same  
25 plating processing tank to perform both of the electroless plating process for forming an initial layer serving as a feeding layer and the electrolytic process for filling the recess. With this method, both of the plating processes can

continuously be performed without changing the processing tank or the plating liquid, for thereby simplifying the apparatus and process while achieving the above effects.

According to the present invention defined in claim 2, there is provided an apparatus for plating a substrate to fill a wiring recess in a semiconductor substrate with plating metal, the apparatus comprising: an electroless plating tank for forming an initial layer on a substrate by electroless plating; an electrolytic plating tank for filling the wiring recess with plating metal while the initial layer serves as a feeding layer; and transfer means for transferring a substrate between the tanks.

With this apparatus, an initial plating layer (seed layer) is formed with an electroless plating process, and then the recess in the substrate is filled with electrolytic plating metal while the initial layer serves as the feeding layer. Accordingly, the recess having a barrier layer of a high electrical resistance can efficiently be filled with a void-free wiring metal, without the sputtering process or the CVD process in a series of plating processes. The electroless plating tank and the electrolytic plating tank should preferably be disposed in close proximity to each other within the same space and separated by a partition.

By providing a substrate transfer means in addition to the electroless tank and the electrolytic plating tank, it is possible to continue from one process to the next process without changing the state of the surface

of the substrate when transferring the substrate. Specifically, the electroless plating tank, the electrolytic plating tank, and required rinse tanks should preferably be arranged in close proximity to each other, and the substrate  
5 should be transferred after the plating process or the rinsing process, without exposing the surface of the substrate to the air. Such a function may also be provided in the transfer means itself.

According to the present invention defined in  
10 claim 3, there is provided a method or apparatus for plating a substrate according to claim 1 or 2, comprising in the electroless plating process or the electroless plating bath: means for disposing a substrate to be plated in such a state that a surface to be processed thereof faces upwardly, and  
15 forming a hermetically sealed space by the surface to be processed; and plating liquid supply means for supplying an electroless plating liquid to the hermetically sealed space to perform an electroless plating process.

By facing the plating surface of the substrate to  
20 be plated upwardly, nitrogen gas bubbles certainly generated in the plating liquid in the electroless plating process will moved upwardly due to buoyancy. Accordingly, the number and the amount of bubbles remaining on the plating surface of the plating substrate and in the fine groove and  
25 hole can be reduced, for thereby reducing the plating defects.

According to the present invention defined in claim 4, there is provided a method or apparatus for plating



a substrate according to claim 3, wherein the minimum amount of electroless plating liquid required for performing a predetermined plating on the substrate to be plated is supplied to the hermetically sealed space, and the electroless plating process is performed with the electroless plating liquid in a static state. Since this method does not move the nitrogen gas bubbles over the plating surface, it is possible to minimize the unevenly plated portions that are generated on the plating surface, as shown in FIG. 17.

According to the present invention defined in claim 5, there is provided a method or apparatus for plating a substrate according to claim 3 or 4, further comprising: pressure pulsation means for generating a pressure in the hermetically sealed space that is higher than atmospheric pressure and for pulsating the pressure.

According to the present invention, since the hydrogen gas bubbles can be encouraged to dissolve into the electroless plating liquid by pressurization, it is possible to encourage the nitrogen gas bubbles to separate from the plating surface. Specifically, the nitrogen gas bubbles attached to the plating surface 97 of the plating substrate W, as shown in FIG. 11A, are contracted by pressurization, as shown in FIG. 11B, to separate from the plating surface 97. The nitrogen gas bubbles 98 are expanded by decompression, as shown in FIG. 11C, to separate completely from the plating surface 97.

According to the present invention defined in

claim 6, there is provided a method or apparatus for plating a substrate according to any one of claims 3 through 5, further comprising a preparation bath disposed in the vicinity of the hermetically sealed space for supplying the minimum amount of prepared electroless plating liquid to the hermetically sealed space just prior to the electroless plating process.

According to the present invention, the plating process is completed before occurrence of problematic reactions specific to the electroless copper plating, such as a Cannizzaro reaction or a disproportionation, which cause deterioration of the plating liquid and changes in concentration of the plating liquid composition immediately after the preparation. Therefore, the plating process can be performed with a highly stable quality.

According to the present invention defined in claim 7, there is provided a method or apparatus for plating a substrate according to claim 6, wherein the electroless plating liquid is processed as a waste liquid without circulating the electroless plating liquid after performing the electroless plating process with the minimum amount of electroless plating liquid.

According to the present invention, since the amount of plating liquid used per deposition (deposition of plating layer) can be maintained to be the minimum required amount, it is possible to avoid increases in cost with the waste liquid and an excessive burden on the environment.

The plating substrate may be held on a turntable

in the electroless plating tank to be rinsed and dried after the plating process. With this arrangement, the plating, rinsing, and drying processes can all be performed in the same area, thereby reducing the space required for device  
5 installation and making the device suitable for installation in a clean room.

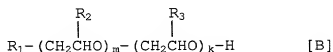
A hot bath for maintaining temperature may be provided in the electroless plating tank in the vicinity of the top of the hermetically sealed space, and a heater for  
10 maintaining temperature may be disposed below the plating substrate. With this arrangement, it is possible to maintain a fixed plating temperature, which is one of the most important factors governing the quality (uniformity of layer thickness, reproducibility, electric conductivity of  
15 the plating layer, etc.) of electroless plating.

In the electroless plating process, the minimum required amount of electroless plating liquid may be set within a range of amount of liquid that includes ions of solutes 1.5 to 20 times as many as a predetermined deposited  
20 metal equivalent. In the electroless plating process, the pressure pulsation means may be configured to generate pressure pulsations having an amplitude of 0 to 1 MPa and a frequency of 0 to 10 Hz.

According to the present invention defined in  
25 claim 8, there is provided a method or apparatus for plating a substrate according to claim 1 or 2, wherein the plating liquid used the electroless plating process or the electroless plating bath comprises copper sulfate ( $\text{CuSO}_4 \cdot$

5H<sub>2</sub>O) having a concentration of 100 to 250 g/l, sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) having a concentration of 10 to 100 g/l, and chlorine ions having a concentration of 0 to 100 mg/l.

According to the present invention defined in claim 9, there is provided a method or apparatus for plating a substrate according to claim 8, wherein the electrolytic plating liquid further comprises at least 0.14 to 70  $\mu$ mol/l of a sulfur compound expressed by a formula in [A] below, 10 to 5000 mg/l of a macromolecular compound expressed in a formula [B] below, and 0.01 to 100 mg/l of a nitrogen compound; wherein L is an alkyl group having a carbon number of 1 to 6 which is substituted by a lower alkyl group, a lower alkoxy group, a hydroxyl group, or a halogen atom; and X is a hydrogen atom, a -SO<sub>3</sub>M group, or a -PO<sub>3</sub>M group (M indicating a hydrogen atom, an alkali metal atom, or an amino group) in the formula [A]; and R1 indicates a residue of a higher alcohol group having a carbon number of 8 to 25, a residue of an alkyl phenol with an alkyl group having a carbon number of 1 to 25, a residue of an alkyl naphthol with an alkyl group having a carbon number of 1 to 25, a residue of a fatty acid amide having a carbon number of 3 to 22, a residue of an alkylamine having a carbon number of 2 to 4, or a hydroxyl group; R2 and R3 indicate a hydrogen atom or a methyl group; and m and k indicate an integer from 1 to 100 in the formula [B].



Since increases in copper concentration in the plating liquid generate proportional increases in the diffusion speed, it is possible to prevent copper ions from becoming diffusion-controlled in the groove and the hole, even when the width of the groove and the diameter of the hole become smaller and the integration in the semiconductor devices increases. Of course, it is also possible to produce a thinner diffusion layer and suppress the current density by agitating the plating liquid.

FIG. 18 is a graph comparing diffusion amount and deposition amount in a hole H of  $1.2 \mu\text{m}$  shown in FIG. 19. In FIG. 18, the vertical axis represents the amount of copper deposition and the amount of copper diffusion (g/s), and the horizontal axis represents the diameter  $\phi$  ( $\mu\text{m}$ ) of the hole H. Here, the diffusion coefficient is set at  $0.72 \times 10^{-9} \text{ m}^2/\text{s}$  and the diffusion layer thickness at  $5 \mu\text{m}$ . When the diffusion amount is greater than the deposition amount, the ions become reaction-controlled to prevent a depletion in copper ions in the hole H and the generation of voids therein. When the diffusion layer is less than the deposition amount, the ions become diffusion-controlled, and voids are generated in the hole H. As seen in FIG. 18, higher concentrations of copper sulfate are advantageous when the hole diameter becomes finer, while the sulfuric acid concentration relatively declines due to the relationship with saturated concentration. By reducing the sulfuric acid concentration, the electrical resistance of the plating liquid increases, improving the uniformity of

the deposited layer thickness.

In FIG. 18, a curve A indicates the diffusion amount (per second) when the copper sulfate concentration is 225 g/l, a curve B indicates the deposition amount (per second) when the current density is 3 A/dm<sup>2</sup>, a curve C indicates the deposition amount (per second) when the current density is 2.5 A/dm<sup>2</sup>, a curve D indicates the deposition amount (per second) when the current density is 2 A/dm<sup>2</sup>, and a curve E indicates the diffusion amount (per second) when the copper sulfate concentration is 75 g/l.

As described above, the plating liquid includes the sulfur compound shown in equation [A] of 0.14 to 40  $\mu$  mol and the macromolecular compound shown in equation [B]. This sulfur compound can achieve a fine deposition. Some examples of these compounds include N, N-dimethyldithiocarbamylpropylsulfonic acid, O-ethyl-S-(3-propylsulfonic acid)-dithiocarbonate, bis-(sulfopropyl) disulfide, and their salts.

In the present invention, the amount of additive in the sulfur compound should preferably be 0.14 to 70  $\mu$  mol/l, since the amount of copper sulfate is greater than the amount of sulfuric acid. The amount of additive in the sulfur compound is less than that in the case where a solution with a low concentration of copper sulfate is used because the cathode vicinity is rich in copper ions, requiring less sulfur compound as an accelerating agent.

Some examples of a macromolecular organic additive contained in the plating liquid are PPG and PEG,

their random or block polymers, or a derivative thereof, such as a polyether type. The amount of macromolecular organic additive is about 10 to 5000 mg/l.

A leveler is added to the above plating liquid to  
5 further control the copper deposition and accelerate plating growth in the bottom of the hole. The leveler is a nitrogen compound containing a polyalkylene imine, such as a phenazine compound, a phthalocyanine compound, a polyethylene imine, and a polybenzyl ethylene imine, or a  
10 derivative thereof, or a thiourea derivative such as an N-dye substitute compound, a safranine compound, such as a phenosafranine, a safranine azo naphthol, a diethyl safranine azo phenol, and a dimethyl safranine dimethyl aniline, or a polyepichlorohydrine or a derivative thereof,  
15 or a phenylthiazonium compound such as a thioflavine, or a amide type, such as an acrylamide, a propylamide, and a polyacrylic acid amide. This nitrogen compound of about 0.01 to 100 mg/l is added as a leveler.

According to the present invention defined in  
20 claim 10, there is provided an apparatus for plating a substrate to fill a wiring recess formed in a semiconductor substrate with plating metal, the apparatus comprising: one processing tank having an electroless plating liquid supply path for supplying an electroless plating liquid to form an  
25 initial layer on a substrate by electroless plating process, and an electrolytic plating liquid supply path for supplying an electrolytic plating liquid to fill the wiring recess by electrolytic plating while the initial layer serves as a

feeding layer; wherein the two paths are selectively switchable.

Hence, an initial plating layer (seed layer) is formed with an electroless plating process, and then the recess in the substrate is filled with electrolytic plating metal while the initial layer serves as the feeding layer. Accordingly, the recess having a barrier layer of a high electrical resistance can efficiently be filled with a void-free wiring metal, without the sputtering process or the CVD process in a series of plating processes. Since both of the electroless plating process for forming the initial layer and the electrolytic plating process for filling the recess can be performed continuously in the same processing tank, the equipment and time required to transfer the substrate can be minimized and the state of the surface of the substrate can be prevented from changing. A cleaning liquid supply path for cleaning a substrate may be disposed to perform a cleaning process in the same processing tank.

The processing tank may hermetically be sealed with a parallel flow. With this arrangement, a plating liquid can flow along the surface of the substrate at a high speed even in a small space to thus perform the efficient plating with sufficient flowability of the plating liquid.

According to the present invention defined in claim 11, there is provided a method or apparatus for plating a substrate according to any one of claims 1 through 10, wherein the plating liquid used in the method or apparatus does not include an alkali metal as a pH



regulator.

### **Brief Description of Drawings**

FIG. 1 is a plan view showing a whole structure  
5 of a plating apparatus according to a first embodiment of  
the present invention;

FIG. 2 is a side view showing a processing tank  
used in the plating apparatus of FIG. 1;

FIG. 3 is a cross-sectional view taken along a  
10 line A-A of the processing tank in FIG. 2;

FIG. 4 is a schematic view showing the processing  
tank used in the plating apparatus in FIG. 1 and circulating  
paths of a processing liquid;

FIG. 5 is a side view of the plating apparatus in  
15 FIG. 1;

FIG. 6 is a flowchart showing processes performed  
with the plating apparatus in FIG. 1;

FIGS. 7A through 7D are schematic diagrams  
explanatory of a process of plating a recess formed in a  
20 substrate;

FIG. 8 is a schematic view showing a processing  
tank used in a plating apparatus according to a second  
embodiment of the present invention;

FIG. 9 is a plan view showing a whole structure  
25 of a plating apparatus according to a third embodiment of  
the present invention;

FIG. 10 is a schematic view showing a structure  
of an electroless plating device in FIG. 9;

FIGS. 11A through 11C are schematic diagrams explanatory of the behavior of hydrogen gas bubbles when pressure of a hermetically sealed space in the electroless plating device is pulsed;

5           FIG. 12 is a schematic view showing a structure of the electroless plating device in FIG. 9;

FIG. 13 is a schematic view showing a structure of an electrolytic plating device in FIG. 9;

10           FIG. 14 is an enlarged view of an area B indicated in FIG. 13;

FIG. 15 is a schematic view showing a processing tank used in the plating apparatus and circulating paths of a processing liquid according to the third embodiment of the present invention;

15           FIGS. 16A and 16B are schematic diagrams explanatory of the behavior of hydrogen gas bubbles in electroless plating, FIG. 16A shows the behavior of the hydrogen gas bubbles when a plating surface of a plating substrate faces downwardly, and FIG. 16B shows the behavior  
20 of the hydrogen gas bubbles when the plating surface of the plating substrate faces sideways;

FIG. 17 is a schematic diagram explanatory of unevenly plated portions generated on a plating surface of a plating substrate by the behavior of hydrogen gas bubbles in  
25 electrolytic plating;

FIG. 18 is a graph comparing diffusion amount and deposition amount in holes formed in a plating substrate; and

FIG. 19 is a schematic view showing an example of a shape of a hole formed in a surface of a plating substrate.

## 5 Best Mode for Carrying Out the Invention

Embodiments according to the present invention will be described below with reference to the accompanying drawings. A plating apparatus is disposed in a rectangular installation frame 10, as shown in FIG. 1. The plating apparatus has a clean zone 13 at one side of the installation frame 10, and load/unload units 14a, 14b and two cleaning and drying devices 60 for post-processing a substrate after the plating process are disposed at the clean zone 13. A transfer device (first transfer robot) 61 for transferring a substrate is provided among the load/unload units 14a, 14b and the cleaning and drying devices 60. The plating apparatus has a contaminated zone 12 at the other side of the installation frame 10, and a second transfer robot 62 movable on a rail is disposed at the central portion of the contaminated zone 12. An  $\text{SnCl}_2$  solution tank 16 containing  $\text{SnCl}_2$  solution used as an activator in plating, a rinse tank 17, a  $\text{PdCl}_2$  solution tank 18 containing  $\text{PdCl}_2$  solution used as a catalyst in electroless plating, and a rinse tank 19 are disposed in order on one side with respect to the second transfer robot 62. An electroless plating tank 20, a rinse tank 21, an electrolytic plating tank 22, and a rinse tank 23 are disposed in order on the other side with respect to the

second transfer robot 62. The rinse tanks 17, 19, 21 and 23 may be provided as needed.

Each of these processing tanks 16-23 has the same basic shape and structure, and comprises a processing  
5 container body 50 having a rectangular plate shape and a recess 50a forming a processing chamber 52 therein, and a cover 51 capable of opening and closing a front opening of the processing container body 50, as shown in FIG. 2. A  
10 packing 53 is mounted at the peripheral portion of the processing container body 50 to maintain the water-tightness of the processing container body 50 when the cover 51 is closed and brought into close contact with the processing container body 50. A holding member for detachably holding  
15 a substrate W is provided on the inner side of the cover 51, and the cover 51 is provided with a sensor (not shown) for detecting the existence of a substrate W on the holding member.

In the processing tank (electrolytic plating tank) 22 for performing electrolytic plating, a plate-like  
20 anode 54 is mounted on the bottom of the recess 50a in the processing container body 50 in parallel with the processing chamber 52, and a shielding plate 55 made of dielectric material is disposed at the opening end of the recess 50a. The shielding plate 55 has an opening 55a therein for  
25 regulating the electric field on a plating surface of the substrate W. The other processing tanks are not provided with the anode 54 or the shielding plate 55.

An upper header 56 and a lower header 57 are

mounted on the top and bottom of the processing container body 50 and communicated with the processing chamber 52 via a plurality of through-holes 56a, 57a, respectively. Thus, for example, a processing liquid is supplied from the lower header 57 to the upper header 56 to thus generate a parallel flow along the surface of the substrate to be plated, as shown in FIG. 3. As shown in FIG. 4, processing liquid circulating devices 33 each having a reservoir tank 31 and a circulating pump 32 are provided below the processing tanks 16-23, and a supply pipe 34 and a return pipe 35 extending from the processing liquid circulating device 33 are connected to the lower header 57 and the upper header 56.

Since, as described above, the plating tanks 20, 22 are hermetically sealed with a parallel flow, a plating liquid can flow along the surface of the substrate at a high speed even in a small space to thus perform the efficient plating with sufficient flowability of the plating liquid. Further, each of the processing tanks 16-23 is vertically positioned, and hence bubbles in fine recesses formed in the substrate W can easily flow out therefrom during the plating process or the like. Therefore, uniformity of the plating reaction and the processing rate can be increased, and simultaneously the installation area of the processing tanks 16-23 can be reduced, resulting in an efficient arrangement of the processing tanks.

In this embodiment, the transfer robot 62 comprises a hexaxial robot having a plurality of arms 63 and a hand 64 which is provided on the end of the arms 63 and is

capable of opening and closing (see FIG. 5). A plurality of rollers 65 are rotatably supported on the inner surface of the hand 64. A temporary holding stage 66 having a plurality of supports is provided in the clean zone 13 and used for temporarily holding a substrate W to be transferred between the clean zone 13 and the contaminated zone 12.

Next, the plating process according to the plating apparatus thus constructed will be described below with reference to FIGS. 6 and 7. The first transfer robot 61 takes out a substrate W held on the load/unload unit 14a, 14b and places the substrate W on the temporary holding stage 66. The second transfer robot 62 transfers the substrate W to the contaminated zone 12, and, when necessary, the substrate W is inserted into the processing container body 50 of the activation tank 16 and activated by a processing liquid containing an activator such as  $\text{SnCl}_2$ . Next, the substrate W is transferred to the adjacent rinse tank 17 to be rinsed, and then transferred to the catalyst application tank 18 to receive a catalyst application.

In this process,  $\text{Sn}^{2+}$  ions from the activator are adsorbed by the surface of the substrate W in the activation tank 16, and these ions are oxidized in the catalyst application tank 18 to be  $\text{Sn}^{4+}$ . On the other hand,  $\text{Pd}^{2+}$  ions are reduced to Pd metal, and the Pd metal is deposited on the surface of the substrate W to serve as a catalyst in the following electroless plating process. A single catalyst containing Pd/Sn colloids may be used in this process. In this embodiment, the catalyst application process described

above is performed in the activation tank 16 and the catalyst application tank 18 belonging to a portion of the plating apparatus. However, the catalyst application process may be performed in a separate apparatus, and then the substrate W may be transferred to the plating apparatus. It is possible to dispense with the activation process and/or the catalyst application process in some cases, depending on a material or a state of the inner surface of the recess formed in the semiconductor substrate.

The second transfer robot 62 further transfers the substrate W to the electroless plating tank 20, where the electroless plating process is performed with a predetermined reducing agent and a predetermined plating liquid. With this process, as shown in FIGS. 7A and 7B, an electroless plating layer 41 is formed on the inner surface of a barrier layer 40. In this case, electrons generated at the solid-liquid interface due to decomposition of the reducing agent are applied to the  $\text{Cu}^{2+}$  via the catalyst on the surface of the substrate, and hence Cu metal is deposited on the catalyst to form the copper layer 41. In addition to Pd, other transition metals such as Fe, Co, Ni, Cu, and Ag may be used as the catalyst.

Next, the substrate W is transferred to the electrolytic plating tank 22 by the transfer robot, and the copper layer 41 formed by the electroless plating process is connected to an electrode to perform the electrolytic plating process with a predetermined plating liquid, for thereby filling the recess 42 with electrolytic plating

metal 43, as shown in FIGS. 7C and 7D.

After the electrolytic plating process is completed, the substrate is taken out by the second transfer robot and transferred to the rinse tank to be rinsed and then placed on a second temporary holding stage 67. The substrate is held by the first transfer robot 61 and transferred to the cleaning and drying device 60 to be cleaned and dried for finishing, and returned to the load/unload unit 14a, 14b. The substrate is finally transferred to a chemical mechanical polishing apparatus (CMP) to remove unnecessary plating metal from the surface of the substrate with the chemical mechanical polishing process.

FIG. 8 shows a plating apparatus according to another embodiment of the present invention. The plating apparatus comprises a vertical processing tank 24 as in the previous embodiment, and processing liquid circulating devices 33a, 33b, 33c for circulating and supplying a respective processing liquid (electroless copper plating liquid, rinse water, and electrolytic copper plating liquid) to the processing tank 24. Supply of the processing liquid can be switched by switching valves 36a through 36c and 37a through 37c. The processing tank 24 comprises a processing container base 50 having an anode and a shielding plate 55 therein, as in the example shown in FIG. 2, and can perform the electrolytic plating process.

In this embodiment, for example, after the electroless plating process is completed, the plating liquid



is returned to the reservoir tank 31a. A rinse water circulating pump 32b is operated to introduce rinse water into the processing tank 24, and then an electrolytic plating liquid is introduced from the reservoir tank 31c into the processing tank 24. After the electrolytic plating process is completed, a rinsing process is similarly performed. Thus, it is possible to eliminate such problems that plating liquids are mixed with each other. In this embodiment, the electroless copper plating process, the rinsing process, the electrolytic copper plating process, the rinsing process, and other processes can continuously be performed in the same processing tank 24 without transferring a substrate, simply by changing processing liquids. Therefore, the present embodiment can decrease the number of the required tanks compared with the previous embodiment and can eliminate the need of a transfer robot for transferring a substrate between tanks, for thereby compacting a installation frame. Further, throughput is increased as the transferring time can be eliminated.

FIG. 9 shows a plating apparatus according to still another embodiment of the present invention. A transferring rail 61a is extended from one side of a rectangular frame to the other side of the frame, and a transfer device (transfer robot) 61 is movably provided on the transferring rail 61a. A load/unload unit 41, a pre-treatment unit 68, an electroless plating unit 69, a first spin drying unit 70A, an electrolytic plating unit 71, and a second spin drying unit 70B are clockwise disposed in order

so that these units surround the transfer robot 61. The pre-treatment unit 68 comprises an activator ( $\text{SnCl}_2$  solution) tank or a catalysis ( $\text{PdCl}_2$  solution) tank, for example.

5           FIG. 10 is a schematic view showing a configurational example of the electroless plating unit 69 shown in FIG. 9. The electroless plating unit 69 has a turntable 72 for holding a substrate W to be plated such as a semiconductor substrate thereon. A heater 73 for  
10 maintaining temperature is provided in the turntable 72, and the turntable 72 can vertically be moved via a ball screw 85 by a motor 86 and rotated via a timing belt 83 by a motor 84.

          A plating cell 92 having an opening in its lower  
15 surface is disposed above the turntable 72, and a seal packing 91 which is brought into close contact with the plating substrate W held by a housing 96 is provided at the outer edge of the lower end of the plating cell 92. Specifically, when the turntable 72 is upwardly moved, a  
20 hermetically sealed space is formed in the plating cell 92 in such a state that the surface of the plating substrate W is brought into close contact with the seal packing 91. The hermetically sealed space has a volume sufficient for accommodating the minimum amount of plating liquid  
25 (electroless plating liquid) required for performing a predetermined plating on the surface of the plating substrate W, as described later.

          A preparation bath 74 is disposed in the vicinity

of the upper portion of the plating cell 92 and supplied with plating liquids A, B, C, and pure water D. An impeller 76a connected to an agitator 76 is disposed in the preparation bath 74, and a heater 81 is disposed in the preparation bath 74. A plating liquid in the preparation bath 74 is supplied to the plating cell 72 via a plating liquid supply valve 79.

A hot bath 75 is disposed in the vicinity of the outer portion of the preparation bath 74 so as to surround the preparation bath 74. An impeller 77a connected to an agitator 77 is disposed in the hot bath 75, and a heater 82 is disposed in the hot bath 75. The reference numeral 80 denotes a plating liquid discharge valve for discharging a plating liquid after the plating process is completed in the plating cell 92. A plating liquid discharged through the plating liquid discharge valve 80 flows into a waste liquid tank 93. The reference numeral 78 denotes a pressure supply valve for supplying pressure into the plating cell 78. The pressure in the plating cell 92 can be pulsed via the pressure supply valve 78 by a pressure pulsation generator 94.

The pressure pulsation generator 94 comprises a pressure regulator valve 87 for high pressure, a pressure regulator valve 88 for low pressure, a switching valve 89 for switching pressure, and a pneumatic pressure source 90, and can generate pressure pulsations having an amplitude of 0 to 1 MPa and a frequency of 0 to 10 Hz. The reference numerals P1, P2 denote pressure gauges.

In the electroless plating apparatus thus constructed, when a substrate W is plated, the plating substrate W is held in a predetermined position on the upper surface of the turntable 72 positioned below the plating cell 92. In this state, the turntable 72 is moved upwardly via the ball screw 85 by the motor 86 to thus bring the upper surface of the plating substrate W into close contact with the seal packing 91, for thereby closing the lower opening of the plating cell 92 to form a hermetically sealed space therein. At this time, the supply valve 79 is opened to supply the plating liquid Q in the preparation bath 74 to the plating cell 92.

The interior of the plating cell 92 has a volume sufficient for accommodating the minimum amount of plating liquid Q required for performing a predetermined plating on the surface of the plating substrate W, and this minimum required amount of plating liquid Q is accommodated in the interior of the plating cell 92. Here, the minimum required amount of electroless plating liquid is set within a range of amount of liquid that includes ions of solutes 1.5 to 20 times as many as a predetermined deposited metal equivalent. In the plating process, the pressure pulsation generator 94 applies a pressure pulsation to the plating cell 92 via the pressure supply valve 8 at a predetermined amplitude and a predetermined frequency.

As shown in FIGS. 11A through 11C, since the plating substrate W is held on the upper surface of the turntable 72 in such a state that the surface to be plated

faces upwardly, hydrogen gas bubbles 98 certainly generated in the plating liquid Q in the electroless plating process is moved upwardly due to buoyancy. Therefore, the number and the amount of bubbles remaining on the plating surface 97 of the plating substrate W and in fine grooves and holes are reduced, for thereby reducing the plating defects. Further, the minimum required amount of plating liquid Q is supplied to the hermetically sealed space in the plating cell 92, and the substrate is plated in a stationary state. Hence, the hydrogen gas bubbles 98 are not moved on the plating surface 87, for thereby minimizing the amount of unevenly plated portions generated on the plating surface.

The pressure of the hermetically sealed space in the plating cell 92 is set to be higher than atmospheric pressure and pulsed by the pressure pulsation generator 94. Hence, as described above, the hydrogen gas bubbles 98 can be encouraged to dissolve into the electroless plating liquid Q by pressurization and simultaneously encouraged to separate from the plating surface 97 by pressure pulsation, as shown in FIGS. 11A through 11C.

The preparation bath 74 is disposed in the vicinity of the upper portion of the plating cell 92, and the minimum required amount of plating liquid prepared in the preparation bath 74 is supplied to the plating cell 92 just before the substrate W is plated. Hence, the plating process is completed before occurrence of problematic reactions specific to the electroless copper plating, such as a Cannizzaro reaction or a disproportionation, which

cause deterioration of the plating liquid and changes in concentration of the plating liquid composition after the preparation. Therefore, the plating process can be performed with a highly stable quality.

5           The plating liquid Q used for plating is discharged from the plating cell 92 via the plating discharge valve 80 into the waste liquid tank 93, where the plating liquid Q is processed as a waste liquid. Hence, the plating process can be performed with a highly stable  
10 quality. In addition, since the amount of plating liquid used per deposition is maintained to be the minimum required amount, it is possible to avoid increases in cost with the waste liquid and an excessive burden on the environment. Further, since the hot bath 75 is disposed above the plating  
15 cell 92 and the heater 73 for maintaining temperature is disposed below the turntable 72, it is possible to maintain a fixed plating temperature, which is one of the most important factors governing the quality (uniformity of layer thickness, reproducibility, electric conductivity of  
20 the plating layer, etc.) of electroless plating.

After the plating process is completed, as described above, the plating liquid discharge valve 80 is opened to discharge the plating liquid in the plating cell 92 to the waste liquid tank 93. The turntable is moved  
25 downwardly via the ball screw 85 by the motor 86, and a cleaning liquid (mainly pure water) is ejected from a cleaning nozzle 95 shown in FIG. 12 to the plating surface of the plating substrate W to clean the plating surface. In

this cleaning process, the cleaning nozzle 95 is swung, and the plating substrate W is slowly rotated via the timing belt 83 by the motor 83. After the cleaning process is completed, the plating substrate W is rotated at a high speed to spin off the cleaning liquid attached to the plating substrate W by centrifugal force.

After a seed layer is formed on the barrier layer in the wiring grooves by the electroless plating process, the substrate W is transferred to the first spin drying unit 70A by the transfer robot 61 and completely dried therein. Then, the substrate W is transferred to the electrolytic plating unit 71, where the electrolytic plating process is performed. The electrolytic plating process will be described below with reference to FIGS. 13 and 14.

As shown in FIG. 13, the electrolytic plating unit 71 comprises a plating tank 110, and the plating tank 110 comprises a plating tank body 111 and a substrate holding member 112 for holding a plating substrate W such as a semiconductor substrate in the plating tank body 111. The substrate holding member 112 has a substrate holding portion 112-1 and a shaft portion 112-2, and the shaft portion 112-2 is rotatably supported in an inner wall of a cylindrical guide member 114 via bearings 115, 115. The guide member 114 and the substrate holding member 112 are vertically movable at a predetermined stroke by a cylinder 116 provided on the top of the plating tank body 111.

The substrate holding member 112 is rotated in a direction indicated by the arrow A via the shaft portion

112-2 by a motor 118 provided on the inner side of the upper portion of the guide member 114. A space C is formed in the substrate holding member 112, and a substrate presser member 117 having a substrate presser portion 117-1 and a shaft portion 117-2 is accommodated in the space C. The substrate presser member 117 is vertically movable at a predetermined stroke by a cylinder 119 provided on the top of the shaft portion 112-2 in the substrate holding member 112.

An opening 112-1a communicating with the space C is formed below the substrate holding portion 112-1 of the substrate holding member 112, and, as shown in FIG. 14, a step portion 112-1b on which the peripheral portion of the plating substrate W is placed is formed at the upper portion of the opening 112-1a. The peripheral portion of the plating substrate W is placed on the step portion 112-1b, and the upper surface of the plating substrate W is pressed by the substrate presser portion 117-1 of the substrate presser member 117, for thereby clamping the peripheral portion of the plating substrate W between the substrate presser portion 117-1 and the step portion 112-1b. The lower surface (plating surface) of the plating substrate W is exposed to the opening 112-1a. FIG. 14 is an enlarged view of the area B indicated in FIG. 13.

A flat plating liquid chamber 120 is provided below the substrate holding portion 112-1 of the plating tank body 111, i.e., below the plating surface of the plating substrate W exposed to the opening 112-1a, and a flat plating liquid introduction chamber 122 is provided



below the plating liquid chamber 120 via a perforated plate 121 having a large number of holes 121a. The recovery gutter 123 for recovering a plating liquid Q overflowing the plating liquid chamber 120 is provided outside of the

5 plating liquid chamber 120.

The plating liquid Q recovered in the recovery gutter 123 is returned to a plating liquid tank 124. The plating liquid Q in the plating liquid tank 124 is horizontally introduced to the plating liquid chamber 120

10 from both sides thereof by a pump 125. The plating liquid Q introduced to the plating liquid chamber 120 from both sides thereof flows vertically into the plating liquid chamber 120 through the holes 121a formed in the perforated plate 121. A distance between the perforated plate 121 and the plating

15 substrate W is set to be 5 to 15 mm. The flow of the plating liquid Q passed through the holes 121a formed in the perforated plate 121 is brought into contact with the plating surface of the plating substrate W in such a state that the plating liquid Q flows upwardly as a uniform flow.

20 The plating liquid Q overflowing the plating liquid chamber 120 is recovered in the recovery gutter 123 and flows into the plating liquid tank 124. Specifically, the plating liquid Q is circulated between the plating liquid chamber 120 in the plating tank body 111 and the plating liquid tank

25 124.

The plating liquid level LQ in the plating liquid chamber 120 is higher than the plating surface level LW of the plating substrate W by a slight distance  $\Delta L$ , and the

plating liquid Q is brought into contact with the whole surface of the plating substrate W.

An electrical contact 127 for electrically connecting with a connecting portion of the plating substrate W is provided in the step portion 112-1b of the substrate holding portion 112-1 in the substrate holding member 112. The electrical contact 127 is connected to a cathode of an external plating power supply (not shown) via a brush 126. An anode 128 is provided on the bottom of the plating liquid introduction chamber 122 in the plating tank body 111, in confrontation with the plating substrate W. The anode 128 is connected to an anode of the plating power supply. A transfer slit 129 for inserting and removing the plating substrate W with a substrate transfer jig such as a robot arm is formed at a predetermined position in the wall of the plating tank body 111.

When the plating process is performed in the electrolytic plating unit thus constructed, the substrate holding member 112 is moved upwardly to a predetermined position (a position at which the plating substrate W held by substrate holding portion 112-1 opposes the transfer slit 129) together with the guide member 114 by actuating the cylinder 116, and simultaneously the substrate presser member 117 is moved upwardly to a predetermined position (a position at which the substrate presser portion 117-1 reaches the upper portion of the transfer slit 129) by actuating the cylinder 119. In this state, the plating substrate W is transferred to the space c in the substrate

holding member 112 by the substrate transfer jig such as a robot arm and placed on the step portion 112-1b in such a state that the plating surface of the plating substrate W faces downwardly. At this state, the substrate presser portion 117-1 is moved downwardly to a position at which the lower surface of the substrate presser portion 117-1 is brought into contact with the upper surface of the plating substrate W, by actuating the cylinder 119, and hence the peripheral portion of the plating substrate W is clamped between the substrate presser portion 117-1 and the step portion 112-1b.

In this state, the substrate holding member 112 is moved downwardly to a position at which the plating surface of the plating substrate W is brought into contact with the plating liquid Q in the plating liquid chamber 120 (a position  $\Delta L$  lower than the plating liquid level  $L_Q$ ) together with the guide member 114 by actuating the cylinder 116. While the substrate holding member 112 is being moved downwardly, the substrate holding member 112 and the plating substrate W are rotated at a low speed by actuating the motor 118. The plating liquid chamber 120 is filled with the plating liquid Q, and the plating liquid passed through the holes 121a formed in the perforated plate flows vertically upwardly in the plating liquid chamber 120. In this state, when a predetermined voltage is applied between the anode 128 and the electric contact 127 by the plating power supply, a plating current flows from the anode 128 to the plating substrate W to form the plating layer on the

plating surface of the plating substrate W.

During the plating process, the substrate holding member 112 and the plating substrate W is rotated at a low speed by actuating the motor 118. This rotation at a low speed is set such that the vertical flow of the plating liquid Q in the plating liquid chamber 120 is not interrupted, and a plating layer having a uniform thickness can be formed on the plating surface of the plating substrate W.

When the plating process is completed, the substrate holding member 112 and the plating substrate W are moved upwardly by actuating the cylinder 116. When the lower surface of the substrate holding portion 112-1 is positioned above the plating liquid level  $L_0$ , the motor 118 rotates the substrate holding member 112 and the plating substrate W at a high speed to spin off the plating liquid attached on the plating surface of the plating substrate W and the lower surface of the substrate holding portion 112-1. After the plating liquid is spun off, the plating substrate W is moved upwardly to a position corresponding to the transfer slit 129. When the substrate presser portion 117-1 is moved upwardly by actuating the cylinder 119, the plating substrate W is released from the substrate presser portion 117-1 in such a state that the plating substrate W is placed on the step portion 112-1b of the substrate holding portion 112-1. In this state, the substrate transfer jig such as a robot arm is inserted from the transfer slit 129 into the space C in the substrate holding

member 112 to pick up the plating substrate W and transfer it to the exterior.

With the electrolytic plating unit 71 thus constructed, a plating substrate W in which holes having a diameter of 0.15  $\mu\text{m}$  and a depth of 1.2  $\mu\text{m}$  were formed was plated by the electrolytic plating process to fill the holes with copper. A plating liquid Q having the following composition, a current density of 2 A/dm<sup>2</sup>, and a temperature of 25 °C was used, and a plating time was set to 150 seconds. The holes were efficiently filled with copper.

Composition of Plating Liquid Q

	CuSO <sub>4</sub> · 5H <sub>2</sub> O	225 g/l		
	H <sub>2</sub> SO <sub>4</sub>	55 g/l		
	Cl <sup>-</sup>	60 mg/l		
15	Sulfur	compound	(N,	N-
	dimethyldithiocarbamylpropylsulfonic acid) 5 mg/l			
	Macromolecular compound (PEG6000)		0.1 g/l	
	Nitrogen compound (safranine compound, janus green B)		2 mg/l	

When a plating liquid having a high concentration of copper sulfate (CuSO<sub>4</sub> · 5H<sub>2</sub>O) is used, as described above, a hole having a diameter of 0.15  $\mu\text{m}$  and a depth of 1.2  $\mu\text{m}$  can efficiently be filled with copper by plating.

FIG. 15 shows a processing tank 25 which can continuously performs an electroless plating process and an electrolytic plating process with the same processing liquid. The processing tank 25 can perform an electrolytic plating process as with the processing tank shown in FIG. 8.

In this processing tank, the electroless plating process is performed, and then the electrolytic plating process is directly performed by energization of a low current of less than  $0.2 \text{ A/dm}^2$ . In this case, an electroless plating liquid is used as a plating liquid, and TMAH is used in place of NaOH or KOH usually used as a pH regulator in the electroless plating process, in order to prevent the semiconductor substrate from being contaminated. TMAH is an organic alkali chemical including a methyl group. It is necessary to avoid using a reducing agent liable to be decomposed, such as formalin, which has commonly been used.

Conventionally, in the through hole plating of the printed circuit board, throwing power has been improved by a high throwing power bath ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  10-80 g/l) having a low Cu concentration. However, when trenches and via holes of a semiconductor substrate are plated, not only throwing power but also levelling of plating is required in order to prevent generation of voids. Further, since the high throwing power bath is easily influenced by the flow of a plating liquid, it is desirable to use a plating liquid having a mid to high increased concentration for reducing the possibility of flow effects.

Various things were examined under the above preconditions. As a result, conventionally used baths such as a  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  low concentration (15-80 g/l) bath (high throwing power bath) superior in throwing power, or a  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  high concentration (150-220 g/l) bath (decorative bath) superior in levelling of plating were found not to be

appropriate. A  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  mid concentration (100-150 g/l) bath was found to be appropriate for a damascene plating process which combines an electroless plating process and an electrolytic plating process of a semiconductor substrate.

- 5 As described above, according to the present invention, an initial plating layer (seed layer) is formed with an electroless plating process, and then the recess in the substrate is filled with electrolytic plating metal while the initial layer serves as the feeding layer.
- 10 Accordingly, the recess having a barrier layer of a high electrical resistance can efficiently be filled with a void-free wiring metal, without the sputtering process or the CVD process in a series of plating processes. Therefore, the present invention can provide a method and apparatus for
- 15 plating a substrate to form wiring by efficiently filling a fine recess formed in a semiconductor substrate with plating metal without a void or contamination.

#### **Industrial Applicability**

- 20 The present invention is suitable for a method and apparatus for plating a substrate to fill a wiring recess formed in a semiconductor substrate with wiring metal such as copper, copper alloy, or the like.

## CLAIMS

1. A method of plating a substrate to fill a wiring recess formed in a semiconductor substrate with  
5 plating metal, said method comprising:

performing an electroless plating process of forming an initial layer on a substrate; and

performing an electrolytic plating process of filling said wiring recess with plating metal while said  
10 initial layer serves as a feeding layer.

2. An apparatus for plating a substrate to fill a wiring recess in a semiconductor substrate with plating metal, said apparatus comprising:

15 an electroless plating tank for forming an initial layer on a substrate by electroless plating;

an electrolytic plating tank for filling said wiring recess with plating metal while said initial layer serves as a feeding layer; and

20 transfer means for transferring a substrate between said tanks.

3. A method or apparatus for plating a substrate according to claim 1 or 2, comprising in said electroless  
25 plating process or said electroless plating bath:

means for disposing a substrate to be plated in such a state that a surface to be processed thereof faces upwardly, and forming a hermetically sealed space by said



surface to be processed; and

plating liquid supply means for supplying an electroless plating liquid to said hermetically sealed space to perform an electroless plating process.

5

4. A method or apparatus for plating a substrate according to claim 3, wherein the minimum amount of electroless plating liquid required for performing a predetermined plating on said substrate to be plated is  
10 supplied to said hermetically sealed space, and the electroless plating process is performed with said electroless plating liquid in a static state.

5. A method or apparatus for plating a substrate  
15 according to claim 3 or 4, further comprising:

pressure pulsation means for generating a pressure in said hermetically sealed space that is higher than atmospheric pressure and for pulsating said pressure.

20 6. A method or apparatus for plating a substrate according to any one of claims 3 through 5, further comprising a preparation bath disposed in the vicinity of said hermetically sealed space for supplying said minimum amount of prepared electroless plating liquid to said  
25 hermetically sealed space just prior to the electroless plating process.

7. A method or apparatus for plating a substrate

according to claim 6, wherein said electroless plating liquid is processed as a waste liquid without circulating said electroless plating liquid after performing the electroless plating process with said minimum amount of  
5 electroless plating liquid.

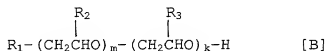
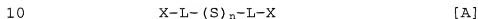
8. A method or apparatus for plating a substrate according to claim 1 or 2, wherein said plating liquid used said electroless plating process or said electroless plating  
10 bath comprises copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) having a concentration of 100 to 250 g/l, sulfuric acid ( $\text{H}_2\text{SO}_4$ ) having a concentration of 10 to 100 g/l, and chlorine ions having a concentration of 0 to 100 mg/l.

9. A method or apparatus for plating a substrate according to claim 8, wherein said electrolytic plating liquid further comprises at least 0.14 to 70  $\mu\text{mol/l}$  of a sulfur compound expressed by a formula in [A] below, 10 to 5000 mg/l of a macromolecular compound expressed in a  
15 formula [B] below, and 0.01 to 100 mg/l of a nitrogen compound;

wherein L is an alkyl group having a carbon number of 1 to 6 which is substituted by a lower alkyl group, a lower alkoxy group, a hydroxyl group, or a halogen  
25 atom; and X is a hydrogen atom, a  $-\text{SO}_3\text{M}$  group, or a  $-\text{PO}_3\text{M}$  group (M indicating a hydrogen atom, an alkali metal atom, or an amino group) in the formula [A]; and

R1 indicates a residue of a higher alcohol group

having a carbon number of 8 to 25, a residue of an alkyl phenol with an alkyl group having a carbon number of 1 to 25, a residue of an alkyl naphthol with an alkyl group having a carbon number of 1 to 25, a residue of a fatty acid amide having a carbon number of 3 to 22, a residue of an alkylamine having a carbon number of 2 to 4, or a hydroxyl group; R2 and R3 indicate a hydrogen atom or a methyl group; and m and k indicate an integer from 1 to 100 in the formula [B].



10. An apparatus for plating a substrate to fill a wiring recess formed in a semiconductor substrate with plating metal, said apparatus comprising:

one processing tank having an electroless plating liquid supply path for supplying an electroless plating liquid to form an initial layer on a substrate by electroless plating process, and an electrolytic plating liquid supply path for supplying an electrolytic plating liquid to fill said wiring recess by electrolytic plating while said initial layer serves as a feeding layer;

wherein the two paths are selectively switchable.

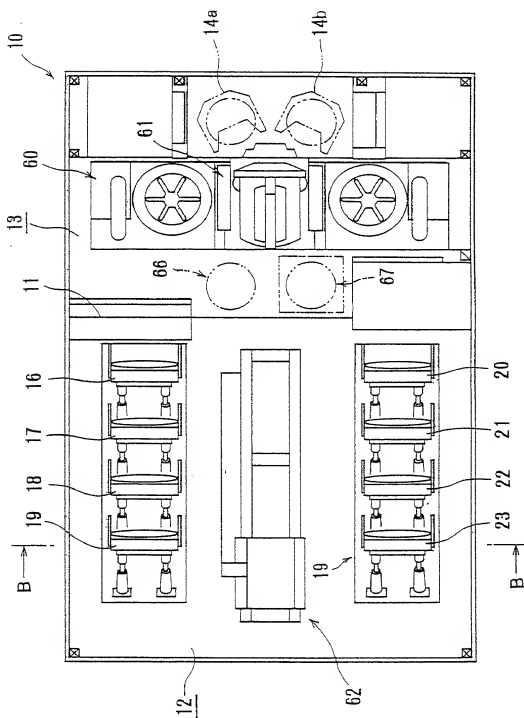
11. A method or apparatus for plating a substrate according to any one of claims 1 through 10, wherein said plating liquid used in said method or apparatus does not

include an alkali metal as a pH regulator.

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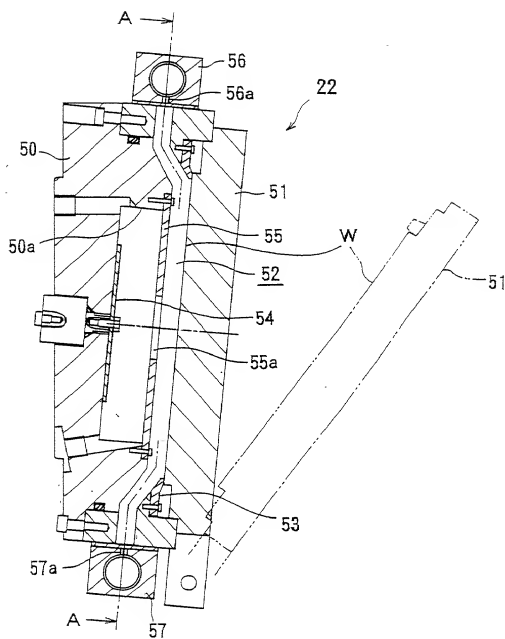
## ABSTRACT

The present invention provides a method and apparatus for plating a substrate to form wiring by  
5 efficiently filling a fine recess (42) formed in a semiconductor substrate (W) with plating metal without a void or contamination. The method for plating a substrate to fill a wiring recess formed in a semiconductor substrate with plating metal (43) comprises performing an electroless  
10 plating process of forming an initial layer (41) on a substrate (W), and performing an electrolytic plating process of filling the wiring recess with plating metal, while the initial layer serves as a feeding layer.



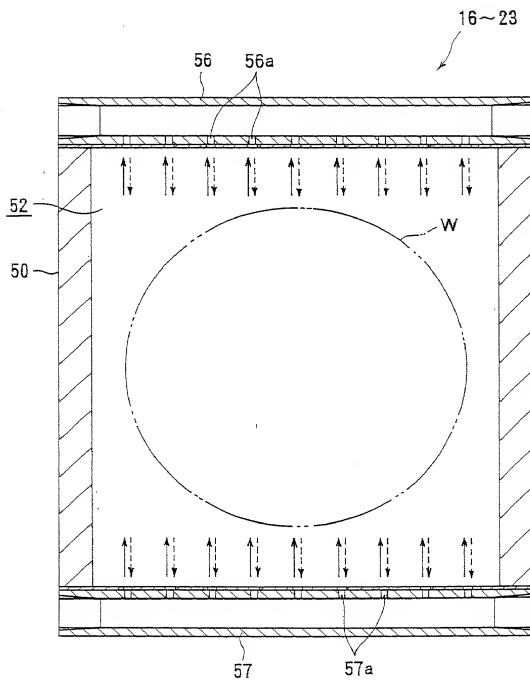
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FIG. 2



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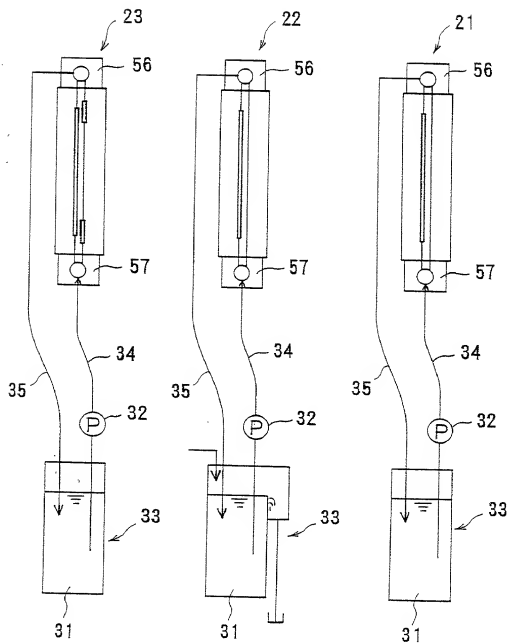
FIG. 3





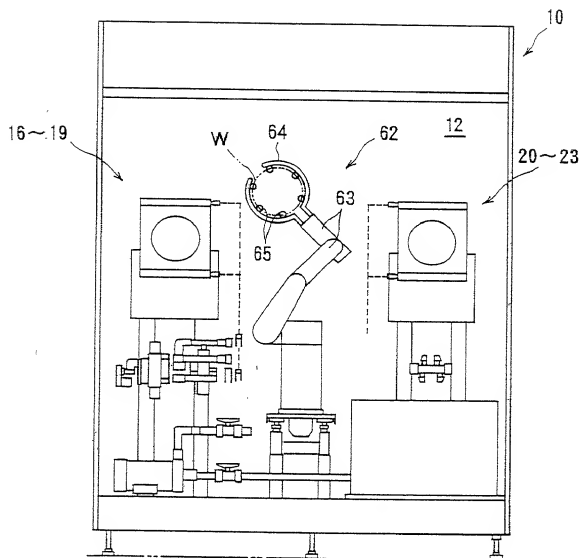
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FIG. 4



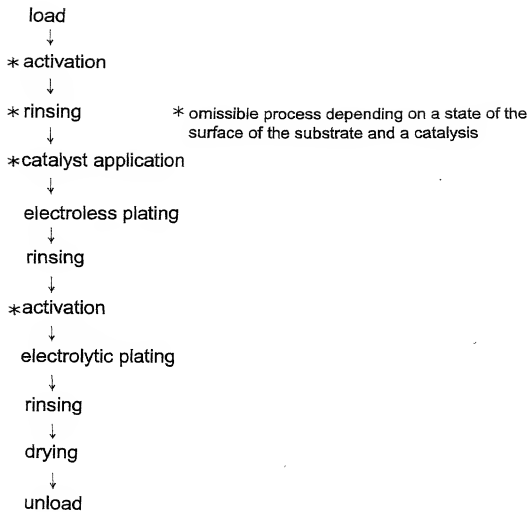
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FIG. 5



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F I G. 6



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FIG. 7A

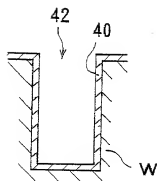


FIG. 7B

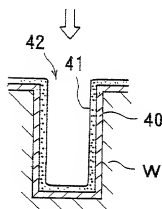


FIG. 7C

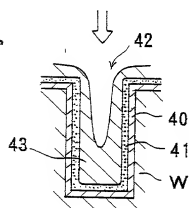
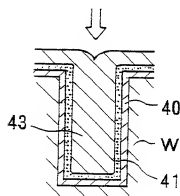
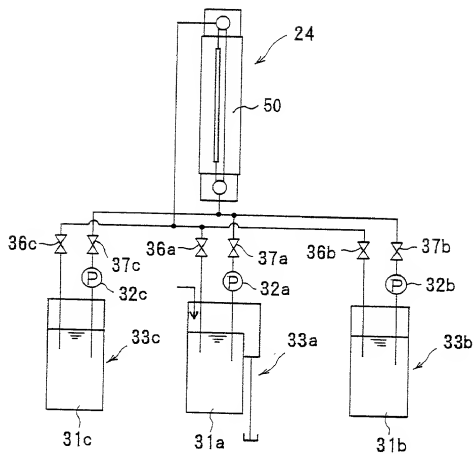


FIG. 7D

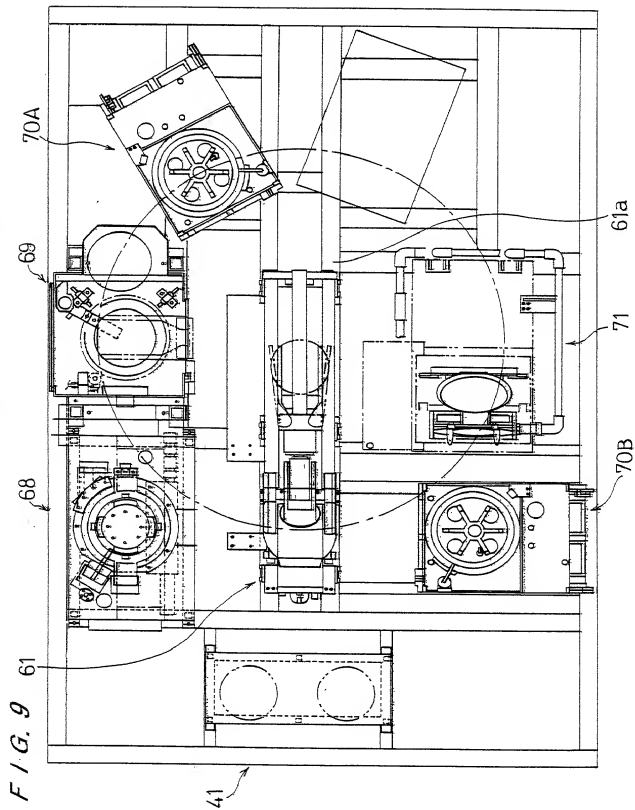


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FIG. 8



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FIG. 10

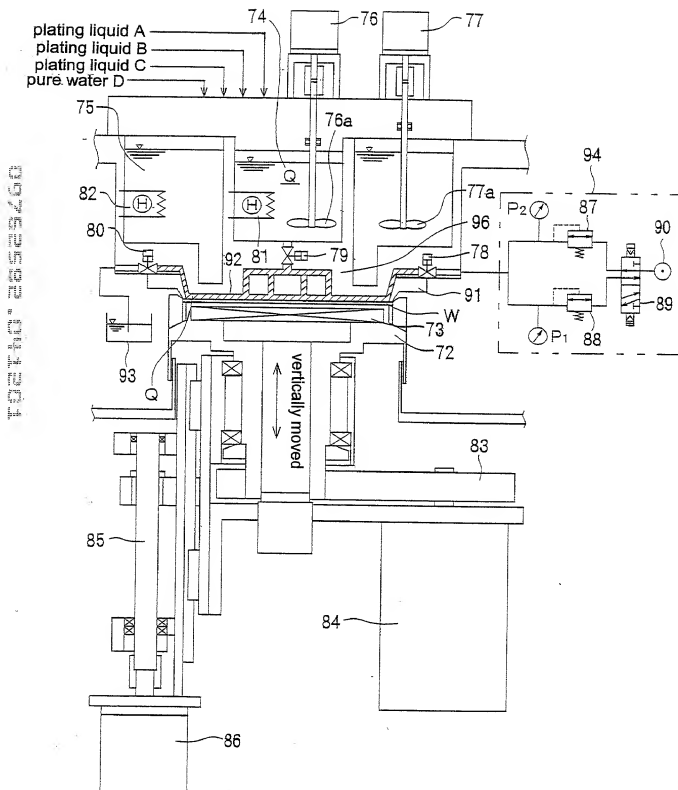


FIG. 11A

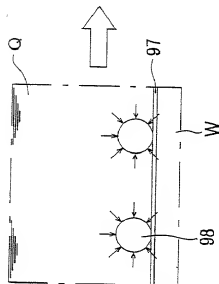


FIG. 11B

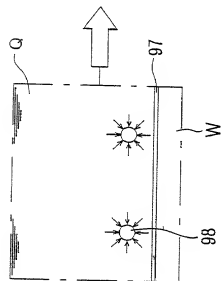
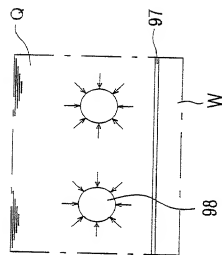


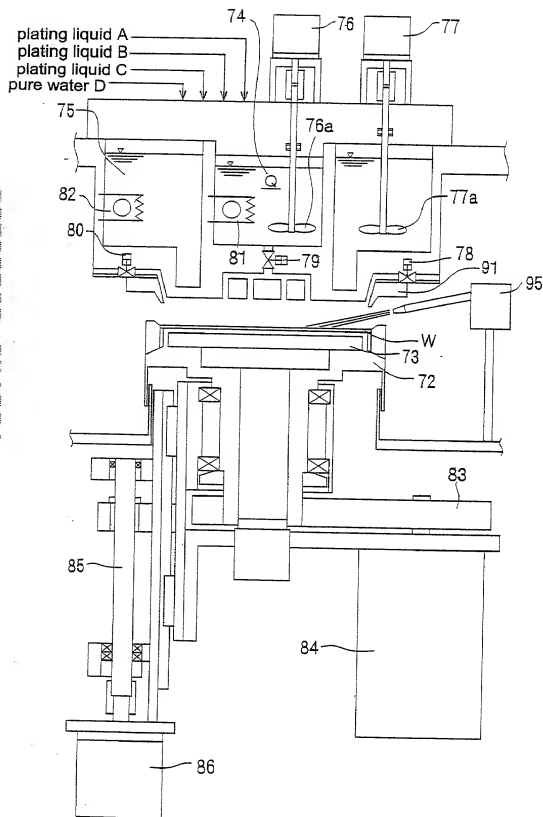
FIG. 11C





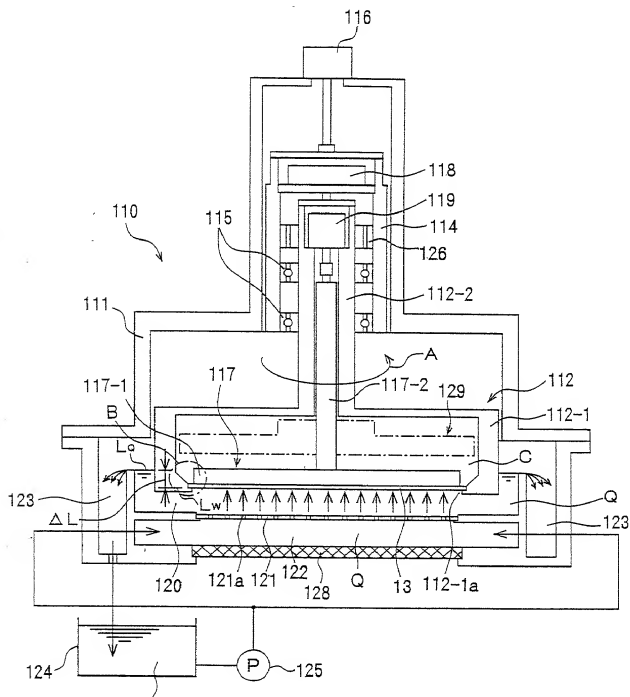
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FIG. 12



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FIG. 13



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FIG. 14

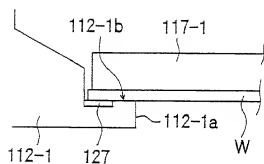
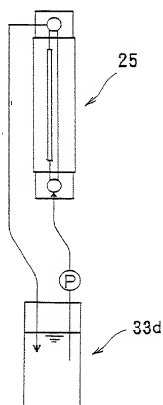


FIG. 15



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FIG. 16A

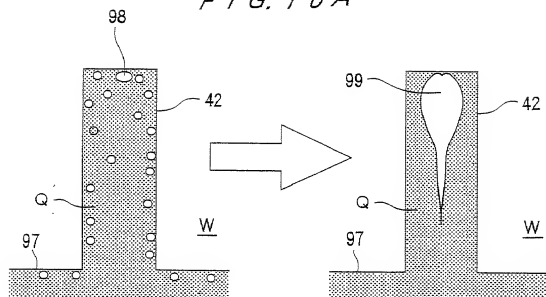
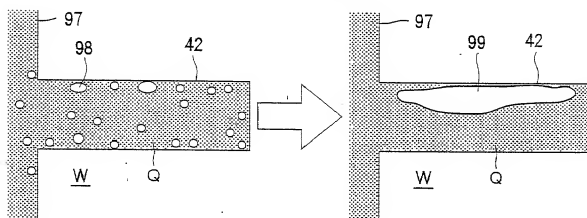
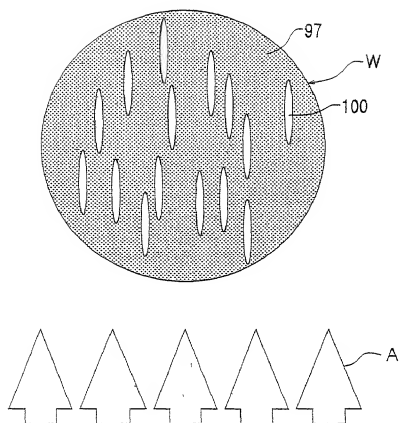


FIG. 16B



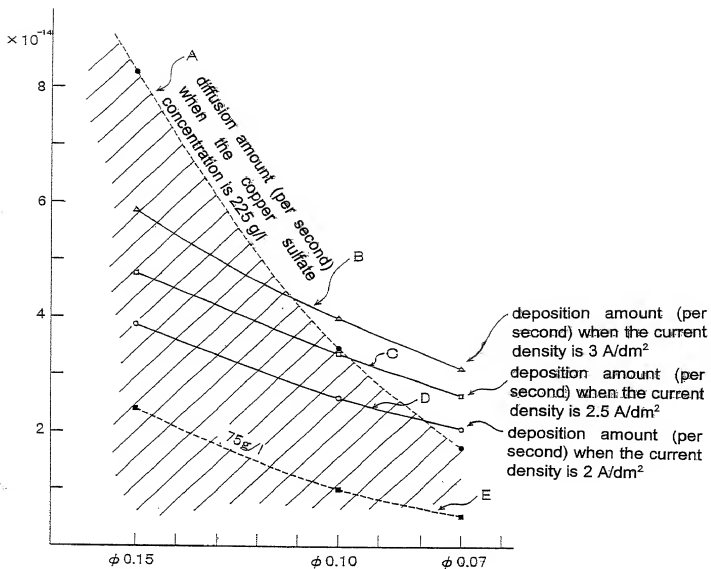
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FIG. 17



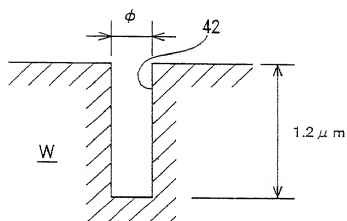
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FIG. 18



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FIG. 19



**DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATION**

( ) Original ( ) Supplemental ( ) Substitute (X) PCT ( ) Design

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; that I verily believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Title: SUBSTRATE PLATING METHOD AND APPARATUS

of which is described and claimed in:

- ( ) the attached specification, or  
 ( ) the specification in the application Serial No. \_\_\_\_\_ filed \_\_\_\_\_;  
 and with amendments through \_\_\_\_\_ (if applicable), or  
 (X) the specification in International Application No. PCT/ JP99/04349, filed August 11, 1999, and as amended  
 on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the content of the above-identified specification, including the claims, as amended by any amendment(s) referred to above.

I acknowledge my duty to disclose to the Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim priority benefits under Title 35, United States Code, §119 (and §172 if this application is for a Design) of any application(s) for patent or inventor's certificate listed below and have also identified below any application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

COUNTRY	APPLICATION NO.	DATE OF FILING	PRIORITY CLAIMED
Japan	10-239490	August 11, 1998	Yes
Japan	11-30230	February 8, 1999	Yes
Japan	11-220363	August 3, 1999	Yes

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application.

APPLICATION SERIAL NO.	U.S. FILING DATE	STATUS: PATENTED, PENDING, ABANDONED



And I hereby appoint Michael R. Davis, Reg. No. 25,134; Matthew M. Jacob, Reg. No. 25,154; Jeffrey Nolton, Reg. No. 25,408; Warren M. Cheek, Jr., Reg. No. 33,367; Nils E. Pedersen, Reg. No. 33,145 and Charles R. Watts, Reg. No. 33,142, who together constitute the firm of WENDEROTH, LIND & PONACK, L.L.P., attorneys to prosecute this application and to transact all business in the U.S. Patent and Trademark Office connected therewith.

I hereby authorize the U.S. attorneys named herein to accept and follow instructions from WATANABE & HOTTA as to any action to be taken in the U.S. Patent and Trademark Office regarding this application without direct communication between the U.S. attorneys and myself. In the event of a change in the persons from whom instructions may be taken, the U.S. attorneys named herein will be so notified by me.

Send Correspondence to

Direct Telephone Calls to:

Client Ref. No. CC0517

WENDEROTH, LIND & PONACK, L.L.P.  
2033 K Street, N.W., Suite 800  
Washington, DC 20006

WENDEROTH, LIND & PONACK, L.L.P.  
Area Code (202) 721-8200

Direct Facsimile Messages to:  
Area Code (202) 721-8250

Full Name of First Inventor <u>1-08</u>	FAMILY NAME <u>HONGO</u>	FIRST GIVEN NAME <u>Akihisa</u>	SECOND GIVEN NAME
Residence & Citizenship	CITY <u>Tokyo J P X</u>	STATE OR COUNTRY <u>Japan</u>	COUNTRY OF CITIZENSHIP <u>Japan</u>
Post Office Address	ADDRESS <u>c/o Ebara Corporation, 11-1, Haneda Ohta-ku, Tokyo 144-8510 Japan</u>	CITY <u>Asahi-cho,</u>	STATE OR COUNTRY <u>ZIP CODE</u>
Full Name of Second Inventor <u>2-08</u>	FAMILY NAME <u>OGURE</u>	FIRST GIVEN NAME <u>Naoaki</u>	SECOND GIVEN NAME
Residence & Citizenship	CITY <u>Tokyo J P X</u>	STATE OR COUNTRY <u>Japan</u>	COUNTRY OF CITIZENSHIP <u>Japan</u>
Post Office Address	ADDRESS <u>c/o Ebara Corporation, 11-1, Haneda Ohta-ku, Tokyo 144-8510 Japan</u>	CITY <u>Asahi-cho,</u>	STATE OR COUNTRY <u>ZIP CODE</u>
Full Name of Third Inventor <u>3-08</u>	FAMILY NAME <u>INOUE</u>	FIRST GIVEN NAME <u>Hiroaki</u>	SECOND GIVEN NAME
Residence & Citizenship	CITY <u>Tokyo J P X</u>	STATE OR COUNTRY <u>Japan</u>	COUNTRY OF CITIZENSHIP <u>Japan</u>
Post Office Address	ADDRESS <u>c/o Ebara Corporation, 11-1, Haneda Ohta-ku, Tokyo 144-8510 Japan</u>	CITY <u>Asahi-cho,</u>	STATE OR COUNTRY <u>ZIP CODE</u>
Full Name of Fourth Inventor <u>4-08</u>	FAMILY NAME <u>SENDAI</u>	FIRST GIVEN NAME <u>Satoshi</u>	SECOND GIVEN NAME
Residence & Citizenship	CITY <u>Tokyo J P X</u>	STATE OR COUNTRY <u>Japan</u>	COUNTRY OF CITIZENSHIP <u>Japan</u>
Post Office Address	ADDRESS <u>c/o Ebara Corporation, 11-1, Haneda Ohta-ku, Tokyo 144-8510 Japan</u>	CITY <u>Asahi-cho,</u>	STATE OR COUNTRY <u>ZIP CODE</u>

Full Name of Fifth Inventor	FAMILY NAME <u>IKEGAMI</u>	FIRST GIVEN NAME <u>Tetsuma</u>	SECOND GIVEN NAME
Residence & Citizenship	CITY <u>Tokyo J P X</u>	STATE OR COUNTRY <u>Japan</u>	COUNTRY OF CITIZENSHIP <u>Japan</u>
Post Office Address	ADDRESS CITY STATE OR COUNTRY ZIP CODE <u>c/o Ebara Corporation, 11-1, Haneda Asahi-cho,</u> <u>Ohta-ku, Tokyo 144-8510 Japan</u>		
Full Name of Sixth Inventor	FAMILY NAME <u>MISHIMA</u>	FIRST GIVEN NAME <u>Koji</u>	SECOND GIVEN NAME
Residence & Citizenship	CITY <u>Tokyo J P X</u>	STATE OR COUNTRY <u>Japan</u>	COUNTRY OF CITIZENSHIP <u>Japan</u>
Post Office Address	ADDRESS CITY STATE OR COUNTRY ZIP CODE <u>c/o Ebara Corporation, 11-1, Haneda Asahi-cho,</u> <u>Ohta-ku, Tokyo 144-8510 Japan</u>		
Full Name of Seventh Inventor	FAMILY NAME <u>OKUYAMA</u>	FIRST GIVEN NAME <u>Shuichi</u>	SECOND GIVEN NAME
Residence & Citizenship	CITY <u>Tokyo J P X</u>	STATE OR COUNTRY <u>Japan</u>	COUNTRY OF CITIZENSHIP <u>Japan</u>
Post Office Address	ADDRESS CITY STATE OR COUNTRY ZIP CODE <u>c/o Ebara Corporation, 11-1, Haneda Asahi-cho,</u> <u>Ohta-ku, Tokyo 144-8510 Japan</u>		

I further declare that all statements made herein of my own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

1st Inventor Akihisa Hongo Akihisa HONGO Date March 30, 2001

2nd Inventor Naoaki Ogure Naoaki OGURE Date March 30, 2001

3rd Inventor Hiroaki Inoue Hiroaki INOUE Date March 30, 2001

4th Inventor Satoshi Sendai Satoshi SENDAI Date March 30, 2001

5th Inventor Tetsuma Ikegami Tetsuma IKEGAMI Date March 30, 2001

6th Inventor Koji Mishima Koji MISHIMA Date March 30, 2001

7th Inventor Shuichi Okuyama Shuichi OKUYAMA Date March 30, 2001

The above application may be more particularly identified as follows:

U.S. Application Serial No. \_\_\_\_\_ Filing Date \_\_\_\_\_

Applicant Reference Number \_\_\_\_\_ Atty Docket No. \_\_\_\_\_

Title of Invention \_\_\_\_\_

Full Name of 8th Inventor	FAMILY NAME <u>NAGAI</u>	FIRST GIVEN NAME <u>Mizuki</u>	SECOND GIVEN NAME
Residence & Citizenship	CITY <u>Tokyo</u> <u>JPX</u>	STATE OR COUNTRY <u>Japan</u>	COUNTRY OF CITIZENSHIP <u>Japan</u>
Post Office Address	ADDRESS c/o Ebara Corporation, 11-1, Haneda Asahi-cho, Ohta-ku, Tokyo 144-8510 Japan		
Full Name of 9th Inventor	FAMILY NAME <u>KIMIZUKA</u>	FIRST GIVEN NAME <u>Ryoichi</u>	SECOND GIVEN NAME
Residence & Citizenship	CITY <u>Tokyo</u> <u>JPX</u>	STATE OR COUNTRY <u>Japan</u>	COUNTRY OF CITIZENSHIP <u>Japan</u>
Post Office Address	ADDRESS 15-6, Matsubara 5-chome, Setagaya-ku, Tokyo 156-0043 Japan		
Full Name of 10th Inventor	FAMILY NAME <u>MARUYAMA</u>	FIRST GIVEN NAME <u>Megumi</u>	SECOND GIVEN NAME
Residence & Citizenship	CITY <u>Kanagawa</u> <u>JPX</u>	STATE OR COUNTRY <u>Japan</u>	COUNTRY OF CITIZENSHIP <u>Japan</u>
Post Office Address	ADDRESS GARDENIA PARK #603, 1-43, Nagatsuda 7-chome, Midori-ku, Yokohama-shi, Kanagawa 226-0027 Japan		

I further declare that all statements made herein of my own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

8th Inventor Mizuki Nagai Mizuki NAGAI Date March 30, 2001

9th Inventor Ryoichi Kimizuka Ryoichi KIMIZUKA Date March 30, 2001

10th Inventor Megumi Maruyama Megumi MARUYAMA Date March 30, 2001

4th Inventor \_\_\_\_\_ Date \_\_\_\_\_

5th Inventor \_\_\_\_\_ Date \_\_\_\_\_

6th Inventor \_\_\_\_\_ Date \_\_\_\_\_

7th Inventor \_\_\_\_\_ Date \_\_\_\_\_

The above application may be more particularly identified as follows:

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